

Infrared Spectroscopy of Laser Irradiated Dental Hard Tissues using the Advanced Light Source

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INTRODUCTION

Infrared lasers are ideally suited for the selective and precise removal of carious dental hard tissue while minimizing the healthy tissue loss. Since the initial investigations of Stern¹ over 30 years ago, several unique laser applications have evolved for dentistry, namely laser ablation of dental hard tissue, caries inhibition treatments by localized surface heating, and surface conditioning for bonding². During high intensity laser irradiation, marked chemical and physical changes may be induced in the irradiated dental enamel. These changes can have profound effects on the laser ablation/drilling process and may lead to a reduction in the ablation rate and efficiency, increase peripheral thermal damage and even lead to stalling without further removal of tissue with subsequent laser pulses. Moreover, thermal decomposition of the mineral can lead to changes in the susceptibility of the modified mineral to organic acids in the oral environment. Morphological changes may result in the formation of loosely attached layers of modified enamel that can delaminate leading to failure during the bonding to restorative materials. Therefore, it is important to thoroughly characterize the laser (thermal) induced chemical and crystalline changes after laser irradiation.

The mineral, hydroxyapatite, found in bone and teeth contains carbonate inclusions that render it highly susceptible to acid dissolution by organic acids generated from bacteria in dental plaque. Upon heating to temperatures in excess of 400 °C, the mineral decomposes to form a new mineral phase that has increased resistance to acid dissolution³. Recent studies suggest that as a side effect of laser ablation, the walls around the periphery of a cavity preparation will be transformed through laser heating into a more acid resistant phase with an enhanced resistance to future decay⁴⁻⁶. However, poorly crystalline non-apatite phases of calcium phosphate may have an opposite effect on plaque acid resistance⁷ and may increase the quantity of poorly attached grains associated with delamination failures.

TISSUE IRRADIATION

A prototype sealed transverse excited atmospheric pressure (TEA) laser (Argus Photonics Group, Jupiter, FL) operating at 9.6 μm with a pulse duration of 8 μs , resonant with the phosphate absorption band of carbonated hydroxyapatite was used to irradiate the specimens. Longitudinal cuts approximately 3 mm long and 200-300 μm across were produced on the enamel surface of 5 x 5 mm² blocks from extracted bovine incisors, polished to a 1 μm finish. Two incisions were made at an incident fluence of 70 J/cm², one with and one without a layer of water. There were 20 laser pulses per spot with overlapping laser spots separated by 50 μm to ensure a smooth intensity profile longitudinally through the incision. The bovine block was scanned using a computer controlled motion control system ESP 300 (Newport, Irvine, CA) with an X-Y stage. Droplets of water were manually applied to the ablation site before each sequence of five laser pulses using a pipette with a volume of 5 μl . The spot profile was single mode and fluences were defined using a Gaussian beam with a $\sim 250 \mu\text{m}$ $1/e^2$ beam diameter. After surface ablation, an Olympus microscope with a maximum magnification of 500 times, interfaced to a digital CCD camera and image analysis software was used to acquire images of the abated enamel.

FTIR spectroscopy in specular reflectance mode is well suited for resolving chemical changes on the surface of enamel⁸. The principal advantage of this technique is that the tissue reflectance is only influenced by a surface layer of a thickness on the order of the wavelength of the light. Thus, surface changes localized to the outer 10 μm of tissue are probed. In previous studies, the area of the carbonate bands centered at 1500 cm⁻¹ were correlated with the transformation of mineral phase to a more acid resistant phase of hydroxyapatite with a marked reduction in the

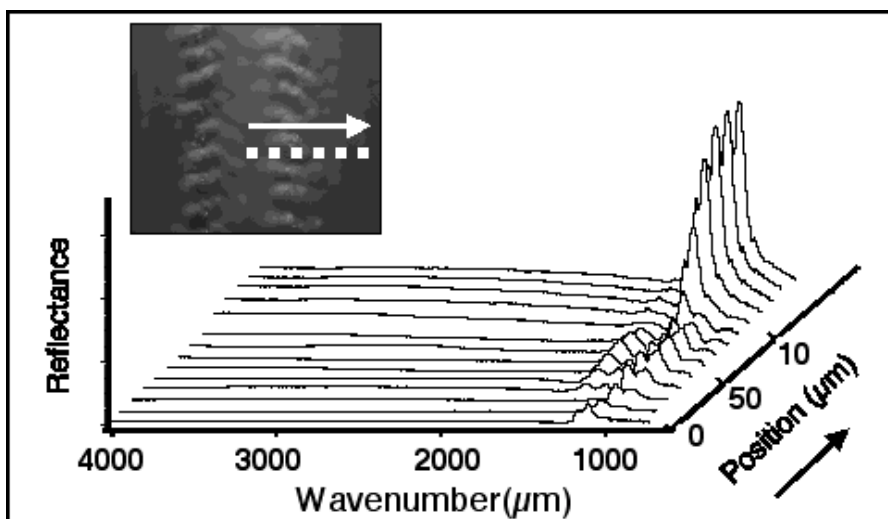


Fig. 1. (Top left image) CO₂ laser produced incision in surface of bovine enamel block at a wavelength of 9.6 μm, pulse duration of 8 μs and fluence of 70 J/cm². FTIR spectra were acquired with a spatial resolution of 10 μm from the center of the incision to the normal enamel. The spectra change markedly across the crater topography.

Advanced Light Source at Lawrence Berkeley National Laboratory was used to acquire spectra of the dental enamel irradiated with the CO₂ laser. Specular reflectance spectra were acquired with a spatial resolution of 10 μm by scanning the 10 μm spot imaged by the FTIR microscope across the laser intensity profile from the center of the laser incision to the normal enamel outside the incision (Figure 1).

RESULTS

Spectra acquired from within different regions of the two laser irradiated areas on the samples with and without an applied water layer are shown in Figs. 1-3. The spectra shown in Fig. 1 indicate that the chemical composition of the irradiated dental enamel varies markedly throughout the different regions of the crater that were exposed to different laser intensity levels. In Fig. 2 we compare two spectra extracted from the transverse scan of Fig. 1. The first spectra represents the normal enamel with the characteristic peaks due to the phosphate group in carbonated hydroxyapatite at 1000 cm⁻¹ and two small peaks near 1500 cm⁻¹ due to the carbonate group. The second spectrum of Fig. 2 was taken 60 μm from the center of the crater and it contains none of the

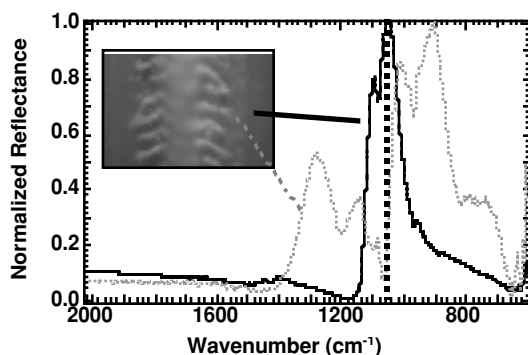


Fig.2. Two spectra taken from different positions in the incision shown in Fig. 1. The normal enamel from outside the crater and the modified enamel 60 μm from the center of the incision are represented by the solid line and the dotted line, respectively. The vertical dotted line at 1041 cm⁻¹ represents the laser wavelength. Note the shift in the absorption maxima

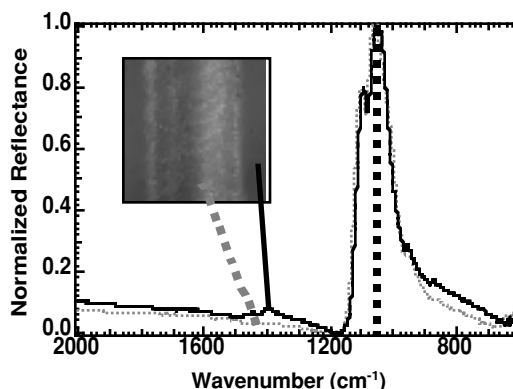


Fig.3. Two spectra taken from different positions in an incision made with an added layer of water. The normal enamel from outside the crater and the modified enamel at the center of the incision are represented by the solid line and the dotted line, respectively

dissolution rate⁸. The incident fluence that was sufficient to induce loss of carbonate in the FTIR spectra coincided with the optimum laser fluence that inhibited both surface and subsurface acid dissolution. Therefore, the FTIR is useful as a nondestructive probe to elucidate the optimum laser parameters to inhibit acid dissolution. The Nicolet Magna 760 FTIR with a Nic-Plan IR microscope equipped with a motorized sample stage, interfaced to beam-line 1.4.3 of the

bands representative of hydroxyapatite, tetra-calcium phosphate or even tri-calcium phosphate phases. Some of the bands are more representative of lower order calcium phosphates such as mono-calcium phosphate. These new bands, to our knowledge have not been previously observed in heat treated or laser irradiated dental hard tissues. However, these non-apatite phases are likely to exhibit higher dissolution rates and be poorly attached to the underlying mineral. Figure 3 shows two spectra taken from an incision produced under the same conditions as the incision shown in Figs. 1 & 2 with a droplet of water added before each sequence of five laser pulses. The first spectrum is of normal enamel and the second is taken from the center of the laser incision. We suspect that the added layer of water aids in preventing the formation of fused areas of the non-apatite phases and results in a more desirable surface morphology. The modified enamel of the walls of the incision is lacking the two carbonate bands located near 1500 cm^{-1} . Removal of the carbonate leaves a hydroxyapatite phase with fewer chemical defects⁸.

Under the appropriate laser irradiation conditions minor chemical and crystalline changes were observed in the enamel. These desirable changes are associated with higher bond strengths to restorative materials and increased resistance to acid dissolution. The non-apatite phases formed after ablation without water may potentially be more susceptible to acid dissolution and be loosely attached to the underlying unaltered enamel substrate leading to poor bonding to restorative materials.

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